<Division of Multidisciplinary Chemistry>Molecular Aggregation Analysis

Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

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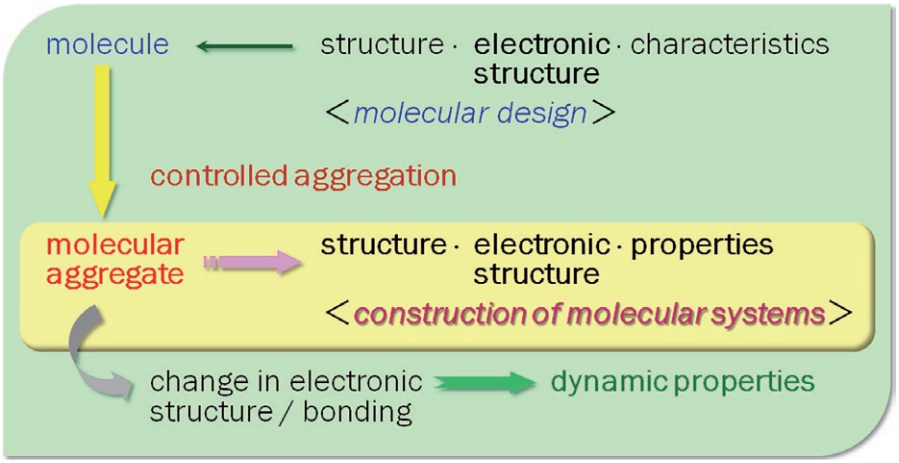
Scope of Research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectrosocpies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous sturcutres in mocrocapsules, boipolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.

KEYWORDS

α-Dispersion
Cell Suspension
Core Level Energy
Film Surface
Organic Semiconductor



Selected Publications

Yoshida, H.; Sato, N., A Precise Analysis of the Core-Level Energy Difference between the Surface and Bulk Region of Organic Semiconductor Thin Films, *J. Phys. Chem. C*, **116,** 10033-10038 (2012).

Yoshida, H.; Ito, E.; Hara, M.; Sato, N., Core Level Energy Differences between the Surface and Bulk of Organic Semiconductor Films: The Effect of Electrostatic Polarization Energy, *Synth. Met.*, **161,** 2549-2553 (2012).

Yoshida, H.; Ito, E.; Hara, M.; Sato, N., Electronic Structure of the Buried Interface between an Organic Semiconductor, *N,N'*-Bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD), and Metal Surfaces, *J. Nanosci. Nanotechnol.*, **12,** 494-498 (2012).

Yoshida, H., Near-Ultraviolet Inverse Photoemission Spectroscopy Using Ultra-Low Energy Electrons, *Chem. Phys. Lett.*, **539-540,** 180-185 (2012).

Daoud, J.; Asami, K.; Rosenberg, L.; Tabrizian, M., Dielectric Spectroscopy for Non-Invasive Monitoring of Epithelial Cell Differentiation within Three Dimensional Scaffolds, *Phys. Med. Biol.*, **57,** 5097-5112 (2012).

Murdey, R.; Sato, N., Voltage Stress Induced Reversible Diode Behavior in Pentacene Thin Films, *J. Chem. Phys.*, **137,** [234703-1]-[234703-5] (2012).

A Precise Analysis of the Core-Level Energy Difference between the Surface and Bulk Regions of Organic Semiconductor Thin Films

We have presented a precise analysis of the angle-resolved X-ray photoemission spectra to evaluate the energy difference for a particular electronic level between the surface and bulk layers of organic thin films. In contrast to the method employed in the earlier studies, the present analysis allows us to determine the energy difference precisely as well as the thickness of the surface region as a result of the following features:

(1) Photoemission spectra were measured at more than 10 different detection angles θ.

(2) Subtle spectral differences were efficiently detected using principal component analysis (PCA).

(3) The determined spectral differences were expressed as the Taylor series expansion of the coefficients of which are calculated by the target transformation of the PCA results without losing information.

(4) By comparing the spectral differences expressed in the form of the Taylor series expansion with the two-layer model, the energy difference of the C1s level between the surface and bulk layers, E_2–E_1, and the thickness of surface layer z are obtained, where E_1 and E_2 are assumed to be the energies of the C1s level in the surface and the other regions in the organic layer, respectively.

The method was applied to the organic films of tris(8-hydroxyquinoline)aluminum (Alq_3), bathocuprine (BCP), and copper phthalocyanine (CuPc) vacuum-deposited on polycrystalline gold surfaces. We determined the energy difference between the surface and the bulk to be ranging from 0.2 to 0.4 eV and the thickness of the surface region to be comparable to that of one monolayer. These values agree with the theoretically estimated values, suggesting that the observed energy difference arises from the difference in the electrostatic polarization energy. The larger energy differences observed for the polar molecules suggest, however, that their permanent dipole moments may also play a role.

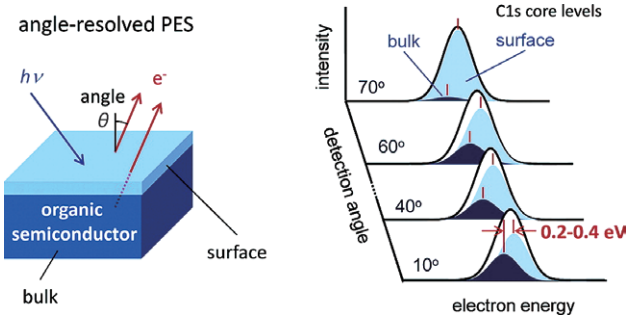


Figure 1. Schematic of angle-resolved photoemission spectroscopy to show core level spectra for an organic semiconductor thin film.

Low-Frequency Dielectric Dispersion of Biological Cell Suspensions

It is known that some cell suspensions show low-frequency dispersion below 10 kHz, which is called α-dispersion. The origin of the α-dispersion has not been well understood and it seems unlikely that all the α-dispersions are interpreted by a unique polarization mechanism. The α-dispersion of bacteria may be due to displacement of counterions around charged cell surfaces, i.e., counterion polarization. The α-dispersion of erythrocyte ghosts (that are erythrocytes lysed in hypotonic media) has been lately interpreted in terms of interfacial polarization by taking into account the presence of a nano-size hole on each ghost. Another candidate for the origin of the α-dispersion is movement of charges and/or reorientation of dipoles in the membranes. To test the possibility erythrocytes were doped with dipicrylamine (DPA) ions that readily translocate in the membrane because of their lipophilic nature. The DPA-doped cell suspensions showed the low-frequency dispersion around a few kHz as expected (Figure 2). The dispersion was accounted for by displacement of the mobile charges in the membrane.

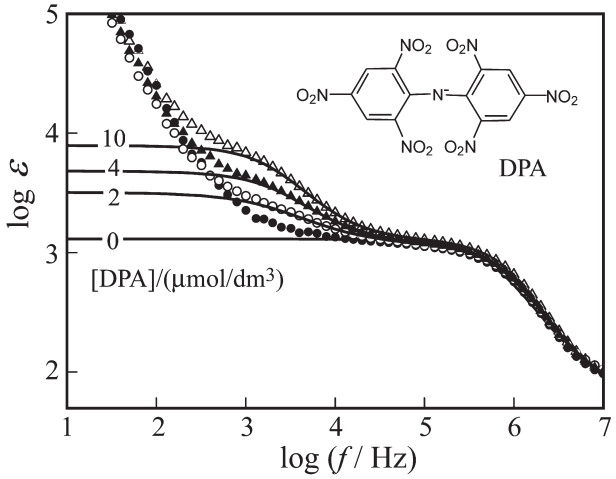


Figure 2. Dielectric spectra of DPA-doped erythrocyte suspensions.